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(54) PREPARATION OF WATER SOLUBLE POLYMER DISPERSIONS FROM VINYLAMIDE MONOMERS

HERSTELLUNG VON WASSERLÖSLICHEN POLYMER- DISPERSIONEN VON VINYLAMID MONOMEREN

PREPARATION DE DISPERSIONS DE POLYMERES HYDROSOLUBLES A PARTIR DE MONOMERES DE VINYLAMIDES

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Description

Field of the Invention

[0001] The present invention relates to a process for the production of a water soluble polymer dispersion from vinylamide monomers, and, more particularly, polymers formed from N-vinylformamide monomers.

Background of the Invention

[0002] One of the problems that has confronted industry in the use of water soluble polymer flocculants is how to dissolve the polymer into water so that it can be utilized for its intended purpose. Early water soluble polymers were provided as dilute aqueous solutions. As the technology improved, and the molecular weights of the polymers were improved, it became increasingly difficult for manufacturers to ship these polymers in solution form because of the high viscosity of even one-half to one percent solutions of the polymers. Manufacturers accordingly started shipping the polymers in the form of commutated solids which could be dissolved into water using various mechanical means. While solving shipment problems, some mechanical means degraded the polymers through shear, and, incomplete dissolution of water soluble polymers, the formation of swollen translucent particles, was common. This led to a waste of polymer, and in some cases, detrimental results such as in the case of so called "fish-eye" particles which caused defects in the manufacture of paper. In the early 1970's water-in-oil emulsions of water soluble polymers were introduced. Using the water-in-oil technology, high molecular weight polymers that rapidly dissolved could be produced, and this technology achieved great acceptance in the water soluble polymer industry. A disadvantage of the water-in-oil emulsion polymer technology however is that the emulsions contain substantial quantities of hydrocarbon liquid. The introduction of hydrocarbon liquids into the systems where these water soluble polymers are used is not always beneficial.

[0003] U.S. 4,929,655 and U.S. 5,006,590 issued to Kyoritsu Yuki Co. Ltd. describe and claim a method for the production of dispersions of water soluble cationic polymers. These polymers were manufactured in an aqueous salt or brine solution in which the polymer was insoluble. The process yielded dispersions of high molecular weight polymers which when added to water would completely dissolve over a relatively short period of time. While an advance to the art, the invention was practical only for preparing water soluble polymer dispersions containing a hydrophobically modified cationic monomer. Of course, anionic polymers which include such functionality cannot be prepared without detracting from the performance of the resultant polymer which is based on the anionic character of the polymer.

[0004] U.S. Patent No. 5,605,970 discloses and claims a method for the manufacture of a particular anionic water soluble polymer in dispersion form. This disclosure teaches that certain anionic polymers, incorporating hydrophobically modified monomers, can be prepared using dispersion polymer methods. The application specifically teaches the manufacture of acrylic acid - ethylhexylacrylate polymers. The ethylhexylacrylate monomer adds a hydrophobic character to the polymer, causing the polymer to become insoluble in certain brine solutions. While these polymers, and the methods for their manufacture are useful, the incorporation of a hydrophobic monomer into a water soluble polymer, where water solubility is desirable is not always advantageous in the final use of the polymer.

[0005] In the process of dispersion polymerization, the monomer and the initiator are both soluble in the polymerization medium, but the medium is a poor solvent for the resulting polymer. Accordingly, the reaction mixture is homogeneous at the onset, and the polymerization is initiated in a homogeneous solution. Depending on the solvency of the medium for the resulting oligomers or macroradicals and macromolecules, phase separation occurs at an early stage. This leads to nucleation and the formation of primary particles called "precursors" and the precursors are colloidally stabilized by adsorption of stabilizers. The particles are believed to be swollen by the polymerization medium and/or the monomer, leading to the formation of particles having a size in the region of $1x10^{-7}$ - $1x10^{-5}$ m (0.1-10.0 microns)

[0006] In any dispersion polymerization, the variables that are usually controlled are the concentrations of the stabilizer, the monomer and the initiator, solvency of the dispersion medium, and the reaction temperature. It has been found that these variables can have a significant effect on the particle size, the molecular weight of the final polymer particles, and the kinetics of the polymerization process.

[0007] Particles produced by dispersion polymerization in the absence of any stabilizer are not sufficiently stable and may coagulate after their formation. Addition of a small percentage of a suitable stabilizer to the polymerization mixture produces stable dispersion particles. Particle stabilization in dispersion polymerization is usually referred to as "steric stabilization". Good stabilizers for dispersion polymerization are polymer or oligomer compounds with low solubility in the polymerization medium and moderate affinity for the polymer particles.

[0008] As the stabilizer concentration is increased, the particle size decreases, which implies that the number of nuclei formed increases with increasing stabilizer concentration. The coagulation nucleation theory very well accounts for the observed dependence of the particle size on stabilizer concentration, since the greater the concentration of the stabilizer adsorbed the slower will be the coagulation step. This results in more precursors becoming mature particles, thus reducing the size of particles produced.

[0009] Dispersion polymers have utility as additives

in various water treatment applications as taught by U. S. Patent Nos. 5,330,650, 5,332,507 and 5,435,922 for example. Furthermore, Japanese Unexamined Patent Publication No. 8-188699 describes an aqueous dispersion composition of a cationic polymer comprising amine or amidine, inorganic salt, nonionic or cationic surface active agent and water. Copolymers formed from the polymerization of various monomers with vinylamine have been described as additives for various water treatment applications such deinking process waters in U. S. Patent No. 5,573,675, dewatering coal tailings in U. S. Patent No. 5.529,588, color removal for pulp and paper applications in U. S. Patent No. 5,476,594, and coal refuse thickening in U. S. Patent No. 5,441,649.

[0010] The polymers described herein will be equally as effective in similar applications.

Summary of the Invention

[0011] The present invention relates to a process for the production of a water soluble polymer dispersion from vinylamide monomers, and, more particularly, polymers formed from N-vinylformamide monomers.

Description of the Invention

[0012] One aspect of this invention is an aqueous dispersion comprising discrete particles of a water-soluble, non-ionic poly(N-vinylamide) polymer obtainable by the polymerization of an N- vinylamide monomer of the following formula:

$$H_2C = CR^2\ NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups. The polymer said N-vinylamide monomer may be selected from the group consisting of N-vinyl formamide, N-methyl-N-vinylacetamide and N-vinyl acetamide.

[0013] Another aspect of the invention is a water-soluble non-ionic dispersion comprising:

discrete particles of a water-soluble, non-ionic poly (N-vinylamide) polymer formed by the polymerization of a N-vinylamide monomer of the formula

$$H_2C = CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups dispersed in an aqueous salt solution, wherein said salt in the salt solution is selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof.

[0014] The invention is also a water-soluble non-ionic dispersion comprising:

discrete particles of a water-soluble poly(N-vinylformamide) polymer dispersed in an aqueous salt solution, wherein said salt in the salt solution is selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof.

[0015] The invention is also a water-soluble non-ionic dispersion comprising:

discrete particles of a water-soluble poly(N-vinylacetamide) polymer dispersed in an aqueous salt solution, wherein said salt in the salt solution is selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof.

[0016] Another aspect of the invention is a dispersion comprising:

discrete particles of a water-soluble, non-ionic poly (N-vinylamide) polymer formed by the polymerization of a vinylamide monomer of the formula

$$H_2C = CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups dispersed in an aqueous salt solution, containing a poly(vinyl alcohol) stabilizer polymer.

[0017] The salt in said salt solution in any of the aspects of this invention may be selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof.

[0018] Another aspect of this invention is a dispersion comprising:

discrete particles of a water-soluble non-ionic poly (N-vinylformamide) polymer dispersed in an aqueous salt solution, containing a poly(vinyl alcohol) stabilizer polymer.

[0019] Moreover the invention is also a dispersion comprising:

discrete particles of a water-soluble non-ionic poly (N-vinylacetamide) polymer dispersed in an aqueous salt solution containing a poly(vinyl alcohol) sta-

bilizer polymer.

[0020] The invention is also an aqueous dispersion of discrete particles of a water-soluble vinyl addition polymer containing an effective stabilizing amount of poly (vinyl alcohol) having a molecular weight of 1,000 to 5,000,000.

[0021] Yet another aspect of this invention is an aqueous dispersion of discrete particles of a water soluble polymer comprising:

a) from 5 to 50 weight percent of a water soluble polymer obtainable by polymerizing under free radical forming conditions at a pH value of from 5 to 8, an N-vinyl formamide monomer;
b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof; and
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ to 25 Pas (10 to 25,000 cps) at 25° C.

[0022] The polymer is preferably dispersed in an aqueous salt solution; wherein the aqueous anionic salt solution is preferably obtained with a salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof.

[0023] In any of the aspects of this invention, the stabilizer polymer may be selected from the group consisting of poly(vinyl alcohol), partially hydrolyzed poly(vinyl acetate), hydrolyzed poly(vinyl acetate/N-vinyl formamide), poly(vinyl alcohol/acrylamide), poly(diallyldimethyl ammonium chloride), poly(dimethylaminoethyl acrylate methyl chloride quaternary salt), poly(dimethylaminoethyl methacrylate methyl chloride quaternary salt), poly(dimethylaminoethyl acrylate benzyl chloride quaternary salt), poly (dimethylaminoethyl methacrylate benzyl chloride quaternary salt), poly(diallyldimethyl ammonium chloride/dimethylaminoethyl acrylate methyl chloride quaternary salt), poly(diallyldimethylammonium chloride/dimethylaminoethyl methacrylate methyl chloride quaternary salt), poly(diallyldimethylammonium chloride/dimethylaminoethyl acrylate benzyl chloride quaternary salt), and poly(diallyldimethyl ammonium chloride/dimethylaminoethyl methacrylate benzyl chloride quaternary salt) and combinations thereof.

[0024] The invention is also a dispersion of discrete particles of a water-soluble copolymer comprising:

a copolymer obtainable by polymerization of a N-vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups; with at least one second monomer selected from the group consisting of vinyl acetate, diallyldimethyl ammonium chloride, vinyl pyrrolidinone, acrylonitrile, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate cetyl chloride quaternary salt, dimethylaminoethyl methacrylate cetyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl chloride quaternary salt, dimethylaminoethylmethacrylate benzyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl sulfate quaternary salt, and combinations thereof; said copolymer dispersed in an aqueous salt solution.

[0025] Moreover, another aspect of this invention is an aqueous dispersion of discrete particles of a water soluble polymer comprising:

a) from 5 to 50 weight percent of a water soluble copolymer obtainable by polymerizing at a pH of from 5 to 8:

i. 1-99 mole percent of a N-vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups; and,
ii. 99-1 mole percent of at least one second monomer selected from the group consisting of vinyl acetate, diallyldimethyl ammonium chloride, vinyl pyrrolidinone, acrylonitrile, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate cetyl chloride quaternary salt, dimethylaminoethyl methacrylate cetyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl chloride quaternary salt, dimethylaminoethylmethacrylate benzyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl sulfate quaternary salt, and combinations thereof; said copolymer dispersed in an aqueous salt solution.

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer

polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof; and
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ to 25 Pas (10 to 25,000 cps) at 25 degrees C.

[0026] A further aspect of this invention is an aqueous dispersion of discrete particles of a water-soluble copolymer comprising:

a copolymer obtainable by polymerization of a vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{10} alkyl groups, aryl groups and alkylaryl groups;

with at least one second monomer selected from the group consisting of acrylic acid and salts thereof, methacrylamide and salts thereof, C_1 - C_{10} N-alkyl acrylamide, C_1 - C_{10} N,N-dialkyl acrylamide, C_1- C_{10} N-alkyl methacrylamide, C_1- C_{10} N, N-dialkyl methacrylamide, N-aryl acrylamide, N,-N-diaryl acrylamide, N-aryl methacrylamide, N-N-diaryl methacrylamide, N-arylalkyl acrylamide, N,N-diallylalkyl acrylamide, N-arylalkyl methacrylamide, N,N-diarylalkyl methacrylamide, maleic anhydride, itaconic acid, vinyl sulfonic acid, styrene sulfonic acid, sodium acrylamido methyl propane sulfonic acid, maleic acid and combinations thereof, said copolymer dispersed in an aqueous salt solution.

[0027] Still another aspect of this invention is an aqueous dispersion of discrete particles of a water soluble polymer comprising:

a) from 5 to 50 weight percent of a water soluble polymer obtainable by polymerizing under free radical forming conditions at a pH value of from 5 to 8:

i. 1-99 mole percent of a N-vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{10} alkyl groups, aryl groups and alkylaryl groups; and,
ii. 99-1 mole percent of at least one vinyl monomer selected from the group consisting of acrylic acid and salts thereof, methacrylamide and salts thereof, C_1 - C_{10} N-alkyl acrylamide, C_1 - C_{10} N,N-dialkyl acrylamide, C_1 - C_{10} N-alkyl methacrylamide, C_1 - C_{10} N, N-dialkyl methacrylamide, N-aryl acrylamide, N,-N-diaryl acrylamide, N-aryl methacrylamide, N-N-diaryl methacrylamide, N-arylalkyl acrylamide, N,N-diallylalkyl acrylamide, N-arylalkyl methacrylamide, N,N-diarylalkyl methacrylamide, maleic anhydride, itaconic acid, vinyl sulfonic acid, styrene sulfonic acid, sodium acrylamido methyl propane sulfonic acid, maleic acid and combinations thereof;

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof; and
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ to 25 Pas (10 to 25,000 cps) at 25 degrees C.

The invention is also a method for preparing an aqueous dispersion of discrete particles of a water soluble copolymer which comprises polymerizing under free radical forming conditions at a pH of from about 5 to about 8:

a) 5-50 weight percent of a mixture containing

i. 1-99 mole percent of a N-vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups; and,
ii 99-1 mole percent of at least one of a water soluble vinyl monomer selected from the group consisting of vinyl acetate, diallyldimethyl ammonium chloride, vinyl pyrrolidinone, acrylonitrile, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate cetyl chloride quaternary salt, dimethylaminoethyl methacrylate cetyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl chloride quaternary salt, dimethylaminoethylmethacrylate benzyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl sulfate quaternary

salt, and combinations thereof; said copolymer dispersed in an aqueous salt solution.

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water-soluble stabilizer polymer having an Intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the total weight of the dispersion of a water soluble salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof; and
d) water;

and then recovering a dispersion of said water soluble polymer, said dispersion being characterized as having a viscosity of less than 25Pas (25,000 cps) at 25 degrees C.

[0028] Moreover, the invention is also a method for preparing an aqueous dispersion of discrete particles of a water-soluble non-ionic homopolymer which comprises polymerizing under free radical forming conditions at a pH of from 5 to 8:

a) from 5 to 50 weight percent of a water soluble polymer obtainable by polymerizing under free radical forming conditions at a pH value of from about 5 to about 8, an N-vinylamide monomer of the formula $H_2C = CR^2NRC(O)R^1$ wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and arylalkyl groups;
b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof; and
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ to 25 Pas (10 to 25,000 cps) at 25° C.

[0029] The N-vinylamide monomer in any of the aspects of this invention may be selected from the group consisting of N-vinylformamide, N-methyl-N-vinylacetamide and N-vinyl acetamide.

[0030] Another aspect of this invention is a method for preparing an aqueous dispersion of discrete particles of a water-soluble non-ionic copolymer which comprises polymerizing under free radical forming conditions at a pH of from 5 to 8:

a) 5-50 weight percent of a mixture containing

i. 1-99 mole percent of a N-vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups; and,
ii 99-1 mole percent of at least one of second vinyl monomer selected from the group consisting of acrylic acid and salts thereof, methacrylamide and salts thereof, C_1 - C_{10} N-alkyl acrylamide, C_1 - C_{10} N,N-dialkyl acrylamide, C_1 - C_{10} N-alkyl methacrylamide, C_1 - C_{10} N, N-dialkyl methacrylamide, N-aryl acrylamide, N,-N-diaryl acrylamide, N-aryl methacrylamide, N-N-diaryl methacrylamide, N-arylalkyl acrylamide, N,N-diallylalkyl acrylamide, N-arylalkyl methacrylamide. N,N-diarylalkyl methacrylamide, maleic anhydride, itaconic acid, vinyl sulfonic acid, styrene sulfonic acid, sodium acrylamido methyl propane sulfonic acid, maleic acid and combinations thereof;

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof; and
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ to 25 Pas (10 to 25,000 cps) at 25 degrees C.

[0031] The invention is also a method for in-situ hydrolysis of a dispersion of discrete particles of a water-soluble polymer having pendant amide groups, said polymer dispersed in an aqueous salt solution comprising the steps of:

a) stirring said dispersion;
b) heating said stirred dispersion to a temperature of from 70°C to 90°C;
c) bubbling HCl gas through said heated dispersion; and,
d) recovering a dispersion of discrete particles of a water-soluble polymer having pendant amine groups.

[0032] Furthermore, the invention is also a method for in-situ hydrolysis of a dispersion of discrete particles of a copolymer obtainable by polymerization of a N-vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{10} alkyl groups, aryl groups and alkylaryl groups;
with at least one monomer selected from the group consisting of acrylic acid and salts thereof, methacrylic acid and salts thereof, C_1 - C_{10} N-alkyl acrylamide, C_1 - C_{10} N,N-dialkyl acrylamide, C_1- C_{10} N-alkyl methacrylamide, C_1 - C_{10} N, N-dialkyl methacrylamide, N-aryl acrylamide, N,-N-diaryl acrylamide, N-aryl methacrylamide, N-N-diaryl methacrylamide, N-arylalkyl acrylamide, N,N-diallylalkyl acrylamide, N-arylalkyl methacrylamide, N,N-diarylalkyl methacrylamide, maleic anhydride, itaconic acid, vinyl sulfonic acid, styrene sulfonic acid, sodium acrylamido methyl propane sulfonic acid, maleic acid and combinations thereof dispersed in an aqueous salt solution comprising the steps of:

a) stirring said dispersion;
b) heating said stirred dispersion to a temperature of from 70°C to 90°C;
c) bubbling HCl gas through said heated dispersion; and,
d) recovering a dispersion of discrete particles of a water-soluble polymer having pendant amine groups.

The invention is also a method for in-situ hydrolysis of a dispersion of discrete particles of a water-soluble non-ionic polymer, said polymer formed by polymerization of an N-vinyl amide monomer of the formula $H_2C = CR_2NRC(O)R^1$ wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and arylalkyl groups, said polymer dispersed in an aqueous salt solution comprising the steps of:

a) stirring said dispersion;
b) heating said stirred dispersion to a temperature of from 70°C to 90°C;
c) bubbling HCl gas through said heated dispersion; and,
d) recovering a dispersion of discrete particles of a water-soluble cationic poiy(vinylamine).

Still another aspect of this invention is a method for in-situ hydrolysis of a dispersion of discrete particles of a water-soluble non-ionic poly(N-vinylformamide) polymer, said polymer dispersed in an aqueous salt solution comprising the steps of:

a) stirring said dispersion;
b) heating said stirred dispersion to a temperature of from 70°C to 90°C;
c) bubbling HCl gas through said heated dispersion; and,
d) recovering a dispersion of discrete particles of a water-soluble cationic poly(vinylamine).

Moreover, the invention is also a method for in-situ hydrolysis of a dispersion of discrete particles of a water-soluble non-ionic poly(N-vinylacetamide) polymer, said polymer dispersed in an aqueous salt solution comprising the steps of:

a) stirring said dispersion;
b) heating said stirred dispersion to a temperature of from 70°C to 90°C;
c) bubbling HCl gas through said heated dispersion; and,
d) recovering a dispersion of discrete particles of a water-soluble cationic poly(vinylamine).

Furthermore, the invention is also a method for clarifying wastewater comprising the step of
adding a water-soluble non-ionic dispersion, said dispersion of discrete particles of a water-soluble, non-ionic poly(N-vinylamide) polymer obtainable by the polymerization of a vinylamide monomer of the formula

$$H_2C = CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl to said waste water. A method for dewatering waste water comprising the step of adding a water-soluble non-ionic dispersion, said dispersion of discrete particles of a water-soluble, non-ionic poly(N-vinylamide) polymer obtainable by the polymerization of a vinylamide monomer of the formula

$$H_2O = CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl to said waste water.

[0033] In any of the aspects of this invention, the waste water describes industrial waste water, industrial process water and municipal waste water. The industrial waste water includes food processing waste water, oily waste water, paper mill waste water, and mining waste water.

[0034] The invention is also a method for clarifying waste water comprising the step of adding a water-soluble non-ionic dispersion, said dispersion of

a copolymer obtainable by polymerization of a vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the

group consisting of hydrogen, C_1 - C_{20} alkyl groups, aryl groups and alkylaryl groups; with at least one monomer selected from the group consisting of vinyl acetate, diallyldimethyl ammonium chloride, vinyl pyrrolidinone, acrylonitrile, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate cetyl chloride quaternary salt, dimethylaminoethyl methacrylate cetyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl chloride quaternary salt, dimethylaminoethylmethacrylate benzyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl sulfate quaternary salt, and combinations thereof; said copolymer being dispersed in an aqueous salt solution, to said waste water.

[0035] Furthermore, the invention is also a method for dewatering waste water comprising the step of adding a water-soluble non-ionic dispersion, said dispersion of a copolymer obtainable by polymerization of a vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C, - C_{20} alkyl groups, aryl groups and alkylaryl groups; with at least one monomer selected from the group consisting of vinyl acetate, diallyldimethyl ammonium chloride, vinyl pyrrolidinone, acrylonitrile, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate cetyl chloride quaternary salt, dimethylaminoethyl methacrylate cetyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl chloride quaternary salt, dimethylaminoethylmethacrylate benzyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl sulfate quaternary salt, and combinations thereof; said copolymer being dispersed in an aqueous salt solution, to said waste water.

[0036] The invention is also a method of clarifying as well as a method of dewatering waste water comprising the step of adding a water-soluble non-ionic dispersion, said dispersion of a copolymer obtainable by polymerization of a vinylamide monomer of the formula

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1 - C_{10} alkyl groups, aryl phenyl groups and alkylaryl groups;

with at least one monomer selected from the group consisting of acrylic acid and salts thereof, methacrylamide and salts thereof, C_1 - C_{10} N-alkyl acrylamide, C_1 - C_{10} N,N-dialkyl acrylamide, C_1- C_{10} N-alkyl methacrylamide, C_1 - C_{10} N, N-dialkyl methacrylamide, N-aryl acrylamide, N,-N-diaryl acrylamide, N-aryl methacrylamide, N-N-diaryl methacrylamide, N-arylalkyl acrylamide, N,N-diallylalkyl acrylamide, N-arylalkyl methacrylamide, N,N-diarylalkyl methacrylamide, maleic anhydride, itaconic acid, vinyl sulfonic acid, styrene sulfonic acid, sodium acrylamido methyl propane sulfonic acid, maleic acid and combinations thereof ; said copolymer being dispersed in an aqueous salt solution, to said waste water.

[0037] The present invention is an aqueous dispersion of a water-soluble polymer composition which have good stability and fluidity. The phrase "good stability" is used herein to mean that the aqueous dispersion does not permanently separate into layers during storage. The phrase "good fluidity" is used herein to mean that the aqueous dispersion has a lower viscosity than aqueous solutions of water-soluble polymers of similar concentrations.

[0038] The aqueous dispersion of a water-soluble nonionic polymeric composition may be prepared by polymerizing a given amount of a water soluble N-vinylamide monomer having the formula:

$$CH_2=CHNRC(O)R^1$$

wherein R and R^1 are each independently selected from a group consisting of hydrogen and an alkyl group having from I to 10 carbon atoms capable of forming a water-soluble polymer in a given amount of an aqueous solution. The nonionic polymeric composition may be a co-polymer containing other monoethylincally unsaturated nonionic monomers. The weight ratio of polymer to the aqueous solution can be adjusted. The resulting product is an aqueous nonionic dispersion having such a form that fine particles containing high molecular weight water soluble nonionic polymer formed from the water soluble vinylamide monomer uniformly dispersed in an aqueous medium. This aqueous dispersion has the property of readily giving a uniform aqueous solution by being diluted with water.

[0039] Copolymers of the instant invention polymerized from a first monomer of the formula $H_2C=CHNRC(O)R^1$ with a second monomer to produce copolymers having mole ratios of from 1:99 to 99:1. A preferred molecular weight range for the homo- and copolymers of this invention is from 500,000 to 5,000,000.

[0040] Substituted (meth)acrylamide monomers may be either straight chained or branched alkyl groups. Applicable monomers include, but are not limited to ethyl hexyl (meth)acrylate, diethylaminopropyl (meth)acrylate, dimethylaminohydroxypropyl (meth)acrylamide, N-isopropyl (meth)acrylamide, N-tert-butyl (meth)acrylamide, N,N-dimethylacrylamide (meth)acrylic acid, and N-isopropyl (meth)acrylamide.

[0041] As utilized herein, the term arylalkyl is meant to encompass benzyl groups and phenethyl groups.

M_w

Pendant amine refers to an NH_2 group which is attached to the main polymer chain.

[0042] The aqueous dispersion in accordance with the present invention, if required in the form of an aqueous solution resulting from dilution with water, can be advantageously used in a number of technological fields as flocculating agents, thickeners, soil conditioners, adhesives, food additives, dispersants, detergents, and additives for medicines or cosmetics.

[0043] In most cases, conventional water-soluble polymers are now commercially available in a powder form. The customers dissolve the polymeric powder in an aqueous medium for actual application. The polymer swells in aqueous medium, and the dispersed particles flocculate. It is typically very difficult to dissolve the conventional polymers in an aqueous medium. It is extremely difficult to prepare a uniform concentrated aqueous solution containing the polymers.

[0044] Moreover, a polymeric powder is often difficult to handle at a water treatment facility. In spite of these difficulties, the conventional polymeric compositions are typically available in powdered form because conventional polymerization methods being used. In addition to inconvenience of use, the production of polymers in powered form is uneconomical. The recovery of polymers in a powered form from an aqueous solution as obtained by conventional polymerization methods includes the costs associated with the evaporation of a large quantity of water and the drying of polymer.

[0045] Additional descriptions of conventional polymerization methods for the production of water-soluble polymers from ethylenically unsaturated monomers are described below.

[0046] In accordance with general conventional methods for producing water soluble polymers, a solution polymerization method is carried out using water as the aqueous medium. These methods have an advantage in that the polymerization can be easily accomplished by using an aqueous solution of a monomer in the presence of a polymerization initiator. By these methods, it is easy to obtain polymers having high molecular weights.

[0047] However, several problems have been associated with these methods, including:

(1) During the polymerization process, it is difficult to remove or otherwise control the heat of reaction.
(2) Productivity of the method can be difficult to increase as the concentration of the monomer in the aqueous solution is frequently limited.
(3) During the polymerization process, the viscosity of the reaction mixture increases markedly, typically yielding a jelly-like product. The jelly-like polymeric material is difficult to handle, and the process used to procure the polymer as a powder involves the steps of recovery, drying, and pulverization.

[0048] In an attempt to avoid these problems, it has been suggested using a precipitation polymerization in which the polymerization would be accomplished in an organic medium which is capable of dissolving the monomer and not the resulting polymer. The resulting polymer would be separated out of solution as a precipitate.

[0049] In a water-in-oil suspension polymerization method, a mixture of a monomer and aqueous medium would be dispersed, using a surface active agent, into an organic medium in which both the monomer and the polymer would be sparingly soluble. Polymerization is carried out once the monomer and aqueous medium are dispersed.

[0050] However, these methods involve problems as well. For example, the use of an organic medium typically makes it difficult to obtain a polymer having a high molecular weight. Moreover, different apparatus is required for the recovery of the organic medium. The resulting polymer does not readily dissolve in the aqueous medium, tending to form a jelly-like mass. Once such a mass has formed, the aqueous medium cannot easily penetrate the mass. thereby requiring considerable periods of time to dissolve the polymer into the aqueous medium.

[0051] In addition to the polymerization method already discussed, another method has been suggested in which a water soluble ethylenically unsaturated monomer is contained in a hydrophobic liquid organic dispersing medium that contains an emulsifier used to form a water-in-oil type emulsion. The monomer is polymerized in the presence of water, thereby forming an oil-in-water type emulsion without separating the polymer. The final product, an oil-in-water emulsion, is used for the actual application.

[0052] However, the method requires a large amount of a water-soluble organic solvent whereby secondary pollution by the organic solvent becomes a problem. In addition, a surface active agent is also required to transform the water-in-oil emulsion into the oil-in-water emulsion. The stability of the dispersion is not sufficient, thereby resulting in coagulation during storage or transportation.

[0053] The present invention is a process for producing an aqueous dispersion of a water soluble polymer free from the problems of the various conventional methods as described above. According to this process, the polymerization is easily accomplished without increasing viscosity while obtaining a high concentration of polymer in an aqueous dispersion in a stable and highly flowable state.

[0054] Using this method, a polymer having a high molecular weight similar to the molecular weight of polymers obtained by the conventional aqueous solution polymerization methods. The polymer obtained by the process of the present invention can be easily diluted with water to form a uniform aqueous solution of polymer without the difficulties associated with polymers in a powder form. The resulting aqueous solution can be used as a flocculating agent and other uses discussed

herein.

[0055] In one embodiment of the present invention is that a relatively large amount of the ethylenically unsaturated monomer (a water soluble vinylamide) is polymerized in an aqueous solution. According to the present invention, an increase in viscosity does not occur during the polymerization process. The resulting product has good stability and fluidity in spite of a relatively high polymer concentration. Moreover the resulting aqueous dispersion can be easily diluted with water to a uniform aqueous solution.

[0056] When, according to the present invention, the water-soluble ethylenically unsaturated monomer (a water soluble vinylamide) is polymerized in the aqueous solution, the resulting water-soluble ethylenic polymer forms a loose water-containing complex without being dissolved in water. Phase separation occurs between the complex and the aqueous phase to form microscopic particles, thereby producing a low viscosity aqueous dispersion.

[0057] The resulting polymer forms as microscopically sized globules which disperse in the aqueous solution, thereby forming a low-viscosity aqueous dispersion. When a sufficient amount of water is added to the resulting aqueous dispersion, the state of phase separation can be easily destroyed to form a uniform aqueous solution.

[0058] The polymerization reaction simply proceeds by the application of heat. In addition, a radical initiator, ultraviolet light, or radial rays may be used in the polymerization process. In performing the present invention, it is especially preferred to use a water soluble radical initiator such as hydrogen peroxide, potassium persulfate and ammonium persulfate, or a so-called redox system composed of such water-soluble radical initiator and a reducing agent such as an amine or sodium bisulphite.

[0059] The initiator is typically used in an amount ranging from about 0.005 to about 10% by weight based on the weight of the ethylenically unsaturated monomer (a water soluble vinylamide). The entire amount of the initiator may be added at the beginning of the polymerization process, or a portion of the initiator may be added at the beginning of the polymerization process with the remaining portion being added during the course of the polymerization process.

[0060] The polymer initiator is preferably selected from the group consisting of 2,2,-azobis(2-amidinopropane)hydrochloride (V-50), 2,2,-azobis(N,N'-dimethylene isobutylamide) dihydrochloride (V-044), ammonium persulfate (APS), ammonium persulfate/sodium meta bisulfite (APS/SBS), and ferric/ascorbic acid. The initiator is typically present in an amount between about 400 to 6,000 ppm based on the monomers used.

[0061] The chain transfer agent is preferably selected from the group consisting of benzyl alcohol, isopropyl alcohol, tertiary amines, sodium bisulfite and sodium formate. The chain transfer agent is typically present in an amount between 5 to 2,000 ppm based on the monomers.

[0062] The polymerization reaction temperature generally ranges from 10° to 100°C, more preferably from 40° to 70°C. The reaction is performed so that the polymerization of the vinylamide monomer is substantially completed. Substantial completion means that the conversion is at least 80%. The time required for this reaction generally ranges from 3 to 10 hours. The polymerization can be performed on a batchwise or on a continuous basis.

[0063] The polymerization process can be effected in a pH range of from 5 - 8. A preferred pH range for polymerization is 6 - 7.5.

[0064] In preparing the aqueous polymer dispersion in accordance with the present invention, inorganic salts soluble in water may be required. Examples of inorganic salts that may be used in the present invention include: chlorides, nitrates, sulfates and phosphates of metals and ammonia. Typical examples of these inorganic salts are sodium chloride, calcium chloride, calcium nitrate, sodium nitrate, ammonium nitrate, potassium sulfate, calcium phosphate, aluminum nitrate, and ferric sulfate.

[0065] These inorganic salts may be used singly or as a mixture of two or more salts. The amount of the inorganic salt to be used in the present invention depends on the amount of the inorganic salt which uniformly dissolves in water. The entire amount of the inorganic salt may be added at the beginning of the polymerization process, or portions of the inorganic salt may be added intermittently at any time during the polymerization process. The inorganic salt may also be added after the polymerization process has ended. As used herein, the term phosphates includes, but is not limited to sodium phosphate and sodium hydrogen phosphate. Preferred salts are sodium nitrate, sodium chloride and ammonium sulfate. If ammonium sulfate is the salt, it should be added only after, and not during the polymerisation.

[0066] Addition of the inorganic salts is helpful to some extent for improving the stability and flowability of the resultant aqueous dispersion. This is presumably because the inorganic salt takes up moisture from the resulting polymer particles to compact and stabilize the individual polymer particles.

[0067] The salt aqueous solutions are generally at a concentration of 15% or more, preferably 20% by weight or more. The salt is typically present during the reaction in an amount between 16.5 to 18 weight % based on batch size. At the end of the reaction more salt, typically in an amount between 0.5 to 5.0 weight %, is added. The amount of salt in the final reaction product is in the range between 18.0 to 22.5% by weight of the final product.

Salz

[0068] The homo- and co-polymers are also compatible with conventional stabilizers such as poly(dimethylaminoethylacrylate methyl chloride quaternary salt). When poly(vinyl alcohol) is the stabilizer polymer, it is preferably to have the polymer of as high a molecular

weight and as hydrolyzed as possible. Herein, Mowiol®, a poly(vinyl alcohol) polymer available from Aldrich Chemical Co., 88% hydrolyzed and with a molecular weight of approximately 125,00 to 135,000 was utilized. Though the degree of hydrolysis may vary, a preferred range of hydrolysis is 70 -80%. A preferred molecular weight range for the poly(vinyl alcohol) is from 100,000 to 200,000.

[0069] The in-situ hydrolysis described herein normally hydrolyzes up to 70% of the amide groups to free amine pendant groups. To achieve a 100% hydrolysis, base must be utilized. Hydrolysis can be effected either by bubbling in HCl gas, or by adding an HCl solution dropwise to the dispersion, with stirring at a temperature of from 70°C to 90°C.

[0070] Conventional processes for the preparation of a water soluble cationic polymer useful as a flocculant include polymerization in an aqueous solution, water-in-oil emulsion polymerization, and suspension polymerization in a hydrophobic solvent. U.S. Patent No. 4,929,655 (Takeda et al.), which was issued on May 29, 1990, provided a novel process for preparing a water soluble polymer dispersion which overcomes the many disadvantages of the stationary polymerization, water-in-oil type emulsion polymerization and suspension polymerization processes.

[0071] Conventional processes for the-preparation of a water soluble cationic polymer useful as a flocculant include polymerization in an aqueous solution, water-in-oil emulsion polymerization, and suspension polymerization in a hydrophobic solvent. U.S. Patent No. 4,929,655 (Takeda et al.), which was issued on May 29,1990, provided a process for preparing a water soluble polymer dispersion which overcomes the many disadvantages of the stationary polymerization, water-in-oil type emulsion polymerization and suspension polymerization processes.

[0072] These dispersions have utility for a wide range of applications. As utilized herein, the term industrial process water is meant to encompass water utilised during the papermaking process. These dispersions also have utility as flocculants in systems such as municipal waste waters, paper mills, chemical processing plants, refineries, and food processing plants among others.

Example 1

[0073] To make a poly(N-vinylformamide) homopolymer dispersion, the following procedure was utllized. To a reaction kettle equipped with a reflux condenser, N_2 dispersion tube, star paddle and turbine and thermocouple, was added N-vinylformamlde monomer (available from Air Products & Chemicals Company, 75g), poly(vinylalcohol) (10% solution, 40g), water (250g) glycerol (6g) and $NaNO_3$ (120g). The solution was stirred and heated to 45°C. The initlator, V-50® (avallable from DuPont Chemical Company) was added to one portion (0.2g 20 ml H_20). As the reaction proceeds, there is an increase in viscosity. A total of 125g of NaCl was added in portions throughout the reaction. The total reaction time is roughly 3 - 3.5 hours. The milky-white dispersion is then stored for further use.

Example 2

[0074] To synthesize a poly(N-vinylformamide/ethyl hexylacrylate) copolymer dispersion, the following procedure was utillsed. To a reaction kettle equipped with a reflux condensor, N_2 dispersion tube, star paddle and turbine and thermocouple, was added N-vinylformamide monomer (available from Air Products & Chemicals Company, 54g), ethylhexylacrylate (available from Aldrich Chemical Company, 3.0g), polyvinylalcohol (10% solution, 30g), water (150g), glycerol (45g) and $NaNO_3$, (40g) Na_2SO_4, NaCl (25 g). The solution was stirred and heated to 45°C. The initiator, V-50® (avalla-ble from DuPont Chemical Company) was added in one portion (0.3g 20 ml H_2O).

[0075] As the reaction proceeds, there is an increase in viscosity. A total of 100g of $(NH_4)_2$ SO_4 was added in portions through the reaction. 200g of water was also added to the reaction mixture. The total reaction time is roughly 3 - 3.5 hours. The milky-white dispersion is then stored for further use. The mole ratio of NVF/ethyl hexylacrylate is from about 99/1 to about 90/10.

Example 3

[0076] To hydrolyze the dispersion polymer, the following procedure was utilized. The dispersion polymer was placed in a round bottom flask and enough water was added to make a 2% solution. A molar equivalent of NaOH was added and the mixture was heated to 80-90°C. for 3 hours. Greater than 90% of the amide groups hydrolyzed to amine groups. A molar equivalent of acid can be used as the hydrolyzing agent. Acid hydrolysis yielded copolymers containing a ratio of amine to amide of 70/30.

Example 4

[0077] To hydrolyze a dispersion polymer, the following alternative procedure could be utilised. The first alternative is a hydrolysis utilising HCl gas. In a three necked flask equipped with a reflux condensor, paddle stirrer, thermocouple and gas dispersion tube, a 100g sample of a polyvinylformamide dispersion (15% active, 0.21 moles) is heated to 50°C. Gaseous HCl (8.0 g, 0.21 moles) is then bubbled into the dispersion over 10 minutes. The reaction mixture is then stirred at 50°C. for 2 hours. The resulting copolymer contained roughly 70 % amine hydrochloride and 30% amide. The amount of acid can be varied to achieve different amine/amide ratios.

[0078] In the second alternative, gaseous ammonia is utilized to effect the hydrolysis in the following fashion. In a three necked flask equipped with a reflux conden-

sor, paddle stirrer, thermocouple and gas dispersion tube, a 300 g sample of a polyvinylformamide dispersion (15% active, 0.62 moles) is heated to 50°C. Gaseous ammonia (10.6 g, 0.62 moles) is then bubbled into the dispersion over 10 minutes. The reaction mixture is then stirred at 70°C. for 3 hours. The resulting polymer should contain ≥ 95% amine. As with the acid, the amount of base can be varied to achieve different amine/amide ratios.

Claims

1. An aqueous dispersion **characterized by** comprising discrete particles of a water-soluble non-ionic polymer obtainable by the polymerization of monomers, said monomers comprising N-vinylamide monomers of the following formula:

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1-C_{20} alkyl groups, aryl groups and alkylaryl groups.

2. The dispersion of claim 1, **characterized in that** said polymer is a non-ionic poly(N-vinylamide) homopolymer and said N-vinylamide monomer is selected from the group consisting of N-vinyl formamide, N-methyl-N-vinylacetamide and N-vinylacetamide.

3. The aqueous dispersion of discrete particles of the non-ionic water soluble homopolymer of claim 2 **characterized by** comprising:

a) from 5 to 50 weight percent of a water soluble polymer obtainable by polymerizing under free radical forming conditions at a pH value of from 5 to about 8, an N-vinyl formamide monomer;
b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt; and
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ Pas (10 cps) to 25 Pas (25,000 cps) at 25°C.

4. The aqueous dispersion of discrete particles of the water-soluble polymer of claim 1, **characterized in that** said polymer is a copolymer comprising: a copolymer obtainable by polymerization of a N-vinylamide monomer of the formula:

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1-C_{20} alkyl groups, aryl groups and alkylaryl groups; with at least one second monomer selected from the group consisting of vinyl acetate, diallyldimethyl ammonium chloride, vinyl pyrrolidinone, acrylonitrile, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate cetyl chloride quaternary salt, dimethylaminoethyl methacrylate cetyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl chloride quaternary salt, dimethylaminoethylmethacrylate benzyl chloride quaternary salt, dimethylaminoethylmethacrylate methyl sulfate quaternary salt, and combinations thereof; said copolymer dispersed in an aqueous salt solution.

5. The aqueous dispersion of claim 4, **characterized in that** said dispersion comprises:

a) from 5 to 50 weight percent of a water soluble copolymer obtainable by polymerizing at a pH of from 5 to 8:

i. 1-99 mole percent of said N-vinylamide monomer
ii. 99-1 mole percent of at least one of said second monomers

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$, of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt; and
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ Pas (10 cps) to 25 Pas (25,000 cps) at 25°C.

6. The aqueous dispersion of discrete particles of a water-soluble polymer of claim 1, **characterized in that** said polymer is a copolymer comprising: a copolymer obtainable by polymerization of a N-vinylamide monomer of the formula:

$$H_2C=CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1-C_{10} alkyl groups, aryl groups and alkylaryl groups;

with at least one second monomer selected from the group consisting of acrylic acid and salts thereof, methacrylamide and salts thereof, C_1-C_{10} N-alkyl acrylamide, C_1-C_{10} N,N-dialkyl acrylamide, C_1-C_{10} N-alkyl methacrylamide, C_1-C_{10} N,N-dialkyl methacrylamide, N-aryl acrylamide, N,-N-diaryl acrylamide, N-aryl methacrylamide, N-N-diaryl methacrylamide, N-arylalkyl acrylamide, N,N-diallylalkyl acrylamide, N-arylalkyl methacrylamide, N, N-diarylalkyl methacrylamide. maleic anhydride, itaconic acid, vinyl sulfonic acid, styrene sulfonic acid, sodium acrylamido methyl propane sulfonic acid, maleic acid and combinations thereof, said copolymer dispersed in an aqueous salt solution.

7. The aqueous dispersion of claim 6, **characterized in that** said water soluble copolymer comprises:

a) from 5 to 50 weight percent of a water soluble copolymer having been prepared by polymerizing under free radical forming conditions at a pH value of from 5 to 8:

i. 1-99 mole percent of said N-vinylamide monomer
ii. 99-1 mole percent of at least one of said second vinyl monomers

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt
d) water,

said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ Pas (10 cps) to 25 Pas (25,000 cps) at 25°C.

8. The method for preparing an aqueous dispersion of discrete particles of said water soluble copolymer of claim 4, **characterized by** comprising the steps of:

polymerizing under free radical forming conditions at a pH of from 5 to 8:

a) 5-50 weight percent of a mixture containing

i. 1-99 mole percent of sald vinylamide monomer
ii. 99-1 mole percent of at least one of a water soluble vinyl monomer

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water-soluble stabilizer polymer having an intrinsic viscosity In 1M $NaNO_3$, of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the total weight of the dispersion of a water soluble salt; and
d) water,

and then recovering a dispersion of said water soluble copolymer, said dispersion being characterized as having a viscosity of less than 25 Pas (25,000 cps) at 25°C.

9. A method for preparing an aqueous dispersion of discrete particles of said water-soluble non-ionic homopolymer of claim 2, **characterized by** comprising the steps of polymerizing under free radical forming conditions at a pH of from 5 to 8:

a) from 5 to 50 weight percent of a water soluble polymer obtainable by polymerizing an N-vinylamide monomer of the formula $H_2O = CR^2NRC(O)R^1$ wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1-C_{20} alkyl groups, aryl groups and arylalkyl groups;
b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabllizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0.1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt; and
d) water,

and then recovering a dispersion of said water soluble homopolymer, said dispersion being characterized as having a bulk Brookfield viscosity of from $1x10^{-2}$ Pas (10 cps) to 25 Pas (25,000 cps) at 25°C.

10. A method for preparing an aqueous dispersion of discrete particles of said water-soluble copolymer of claim 6, **characterized by** comprising polymerizing under free radical forming conditions at a pH of from 5 to 8:

a) 5-50 weight percent of a mixture containing

I. 1-99 mole percent of said N-vinylamide monomer
ii. 99-1 mole percent of at least one of said second vinyl monomers

b) from 0.1 to 5 weight percent based on the total weight of the dispersion of a water soluble stabilizer polymer having an intrinsic viscosity in 1M $NaNO_3$ of from 0-1-10 dl/g;
c) from 5 to 40 weight percent based on the weight of the dispersion of a water soluble salt; and
d) water,

and then recovering a dispersion of said water-soluble copolymer, said dispersion being characterlzed as having a bulk Brookfield viscosity of from $1x10^{-2}$ Pas (10 cps) to 25 Pas (25,000 cps) at 25°C.

11. The dispersion of claims 1-10, **characterized in that** said polymer is dispersed in an aqueous salt solution; wherein said aqueous anionic salt solution is formed with a salt selected from the group consisting of ammonium, alkali metal and alkaline earth metal halides, sulfates, phosphates, nitrates and combinations thereof.

12. The dispersion of claims 1 and 2, **characterized in that** said dispersion further comprises a stabilizer polymer; wherein said stabilizer polymer is selected from the group consisting of poly(vinyl alcohol), partially hydrolyzed poly(vinylacetate), hydrolyzed poly (vinylacetate/N-vinyl formamide), poly(vinyl alcohol/acrylamide), poly(diallyldimethylammonium chloride), poly(dimethylaminoethyl acrylate methyl chloride quaternary salt), poly(dimethylaminoethyl methacrylate methyl chloride quaternary salt), poly (dimethylaminoethyl acrylate benzyl chloride quaternary salt), poly(dimethylaminoethyl methacrylate benzyl chloride quaternary salt), poly (diallyldimethylammonium chloride/dimethylaminoethyl acrylate methyl chloride quaternary salt), poly(diallyldimethylammonium chloride/dimethylaminoethyl methacrylate methyl chloride quaternary salt), poly(diallyldimethylammonium chloride/dimethylaminoethyl acrylate benzyl chloride quaternary salt), and poly (diallyldimethylammonium chloride/dimethylaminoethyl methacrylate benzyl chloride quaternary salt) and combinations thereof.

13. The dispersion of any of claims 3-10, **characterized in that** said stabilizer polymer is selected from the group consisting of poly(vinyl alcohol), partially hydrolyzed poly(vinylacetate), hydrolyzed poly(vinylacetate/N-vinyl formamide), poly(vinyl alcohol/acrylamide), poly (diallyldimethylammonium chloride), poly (dimethylaminoethyl acrylate methyl chloride quaternary salt), poly(dimethylaminoethyl methacrylate methyl chloride quaternary salt), poly (dimethylaminoethyl acrylate benzyl chloride quaternary salt), poly(dimethylaminoethyl methacrylate benzyl chloride quaternary salt), poly(diallyldimethylammonium chloride/dimethylaminoethyl acrylate methyl chloride quaternary salt), poly(diallyldimethylammonium chloride/dimethylaminoethyl methacrylate methyl chloride quaternary salt), poly(diallyldimethylammonium chloride/dimethylaminoethyl acrylate benzyl chloride quaternary salt), and poly (diallyldimethylammonium chloride/dimethylaminoethyl methacrylate benzyl chloride quaternary salt) and combinations thereof.

14. A method for in-situ hydrolysis of a dispersion of discrete particles of the water-soluble polymer of claim 1, **characterized in that** said polymer has pendant amide groups, said polymer dispersed in an aqueous salt solution comprising the steps of:

a) stirring said dispersion;
b) heating said stirred dispersion to a temperature of from 70°C to 90°C;
c) bubbling HCl gas through said heated dispersion; and,
d) recovering a dispersion of discrete particles of a water-soluble polymer having pendant amine groups.

15. A method for in-situ hydrolysis of a dispersion of discrete particles of a copolymer of claim 6, **characterized by** comprising the steps of:

a) stirring said dispersion;
b) heating said stirred dispersion to a temperature of from 70°C to 90°C;
c) bubbling HCl gas through said heated dispersion; and,
d) recovering a dispersion of discrete particles of a water-soluble polymer having pendant amine groups.

16. A method for clarifying wastewater **characterised by** comprising the step of adding water-soluble, non-ionic dispersion of claim 2, said dispersion of discrete particles of a water-soluble, non-ionic poly (N-vinylamide) polymer obtainable by the polymerization of a N-vinylamide monomer of the formula:

$$H_2C{=}CR^2NRC(O)R^1$$

wherein R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1-C_{20} alkyl groups, aryl groups and alkylaryl to said waste water.

17. A method for dewatering waste water **characterized by** comprising the step of adding the water-soluble non-ionic dispersion of claim 2, said dispersion of discrete particles of a water-soluble, non-ionic poly (N-vinylamide) polymer obtainable by the polymerization of a vinylamide monomer of the formula:

$$H_2C=CR^2NRC(O)R^1$$

whereln R, R^1 and R^2 are each selected from the group consisting of hydrogen, C_1-C_{20} alkyl groups, aryl groups and alkylaryl to said waste water.

18. A method for clarifying waste water **characterized by** comprising the step of adding the water-soluble dispersion of claim 4; said copolymer being dispersed in an aqueous salt solution, to said waste water.

19. A method for dewatering waste water **characterlzed by** comprisIng the step of adding the water-soluble dispersion of claim 4; said copolymer beIng dispersed in an aqueous salt solution, to said waste water.

20. A method for clarifying waste water **characterized by** comprising the step of adding the water-soluble dispersion of claim 6; said copolymer dispersed in an aqueous salt solution, to said waste water.

21. A method of dewatering waste water **characterized by** comprising the step of adding the water-soluble non-ionic dispersion of claim 6; said copolymer dispersed in an aqueous salt solution, to said waste water.

22. The method of any of claims 16-21, **characterized in that** said waste water is selected from the group consisting of industrial waste water, industrial process water and municipal waste water.

23. The method of claim 22, **characterized in that** said industrial waste water is selected from the group consisting of food processing waste water, oily waste water, paper mill waste water, and mining waste water.

Patentansprüche

1. Wäßrige Dispersion, **dadurch gekennzeichnet, daß** sie getrennte Partikel eines wasserlöslichen nichtionischen Polymers enthält, das durch die Polymerisation von Monomeren erhältlich ist, welche N-Vinylamidmonomere der folgenden Formel

$$H_2C=CR^2NRC(O)R^1$$

umfassen, wobei R, R^1 und R^2 jeweils aus der Gruppe ausgewählt sind, die aus Wasserstoff, C_1-C_{20}-Alkylgruppen, Arylgruppen und Alkylarylgruppen besteht.

2. Dispersion nach Anspruch 1, **dadurch gekennzeichnet, daß** das Polymer ein nichtionisches Poly (Nvinylamid)homopolymer ist und daß das N-Vinylamidmonomer aus der Gruppe ausgewählt ist, die aus N-Vinylformamid, N-Methyl-N-vinylacetamid und N-Vinylacetamid besteht.

3. Wäßrige Dispersion von getrennten Partikeln des nichtionischen, wasserlöslichen Homopolymers nach Anspruch 2, **dadurch gekennzeichnet, daß** sie enthält:

a) 5 bis 50 Gew.% eines wasserlöslichen Polymers, das durch Polymerisation eines N-Vinylformamidmonomers unter freie Radikale bildenden Bedingungen bei einem pH-Wert von 5 bis etwa 8 erhältlich ist;

b) 0,1 bis 5 Gew.% auf der Basis des Gesamtgewichtes der Dispersion eines wasserlöslichen Stabilisatorpolymers mit einer inneren Viskosität in 1M $NaNO_3$ von 0,1-10 dl/g;

c) 5 bis 40 Gew.% auf der Basis des Gewichtes der Dispersion eines wasserlöslichen Salzes; und

d) Wasser,

wobei die Dispersion **dadurch gekennzeichnet ist, daß** sie eine Brookfield-Volumenviskosität von $1x10^{-2}$ Pas (10 cps) bis 25 Pas (25.000 cps) bei 25 °C besitzt.

4. Wäßrige Dispersion von getrennten Partikeln des wasserlöslichen Polymers nach Anspruch 1, **dadurch. gekennzeichnet, daß** das Polymer ein Copolymer ist, das umfaßt:

ein Copolymer, das durch Polymerisation eines N-Vinylamidmonomers der Formel

$$H_2C=CR^2NRC(O)R^1$$

wobei R, R^1 und R^2 jeweils aus der Gruppe ausgewählt sind, die aus Wasserstoff, C_1-C_{20}-Alkylgruppen, Arylgruppen und Alkylarylgruppen besteht, mit mindestens einem zweiten Monomer erhältlich ist, das aus der Gruppe ausgewählt ist, die aus Vinylacetat, Diallyldimethylammoniumchlorid, Vinylpyrrolidinon, Acrylnitril, quatemärem Dimethylaminoethylacrylat-, methylchloridsalz, quaternärem Dimethylaminoethylacrylatbenzylchloridsalz, quaternärem Dimethylaminoethylacrylatmethylsulfatsalz, quaternärem Dimethylaminoethylacrylatcetylchloridsalz, quaternärem

Dimethylaminoethylmethacrylatcetylchlorid-salz, quaternärem Dimethylaminoethylmethacrylatmethylchloridsalz, quaternärem Dimethylaminoethylmethacrylatbenzylchlorid-salz, quaternärem Dimethylaminoethylmethacrylatmethylsulfatsalz und Kombinationen hiervon besteht, wobei das Copolymer in einer wäßrigen Salzlösung dispergiert ist.

5. Wäßrige Dispersion nach Anspruch 4, **dadurch gekennzeichnet, daß** sie enthält:

a) 5 bis 50 Gew.% eines wasserlöslichen Copolymers, das durch Polymerisieren von

i. 1-99 Mol% des N-Vinylamidmonomers und

ii. 99-1 Mol% von mindestens einem der zweiten Monomeren

bei einem pH von 5 bis 8 erhältlich ist,

b) 0,1 bis 5 Gew.% auf der Basis des Gesamtgewichtes der Dispersion eines wasserlöslichen Stabilisatorpolymers mit einer inneren Viskosität in 1M $NaNO_3$ von 0,1-10 dl/g;

c) 5 bis 40 Gew.% auf der Basis des Gewichtes der Dispersion eines wasserlöslichen Salzes; und

d) Wasser,

wobei die Dispersion **dadurch gekennzeichnet ist, daß** sie eine Brookfield-Volumenviskosität von $1x10^{-2}$ Pas (10 cps) bis 25 Pas (25.000 cps) bei 25 °C besitzt.

6. Wäßrige Dispersion von getrennten Partikeln eines wasserlöslichen Polymers nach Anspruch 1, **dadurch gekennzeichnet, daß** das Polymer ein Copolymer ist, das umfaßt:

ein durch Polymerisation eines N-Vinylamidmonomers der Formel

$$H_2C=CR^2NRC(O)R^1$$

worin R, R^1 und R^2 jeweils aus der Gruppe ausgewählt sind, die aus Wasserstoff, C_1-C_{10}-Alkylgruppen, Arylgruppen und Alkylarylgruppen besteht; mit mindestens einem zweiten Monomer, das aus der Gruppe ausgewählt ist, die aus Acrylsäure sowie Salzen hiervon, Methacrylamid und Salzen hiervon, C_1-C_{10}-N-Alkylacrylamid, C_1-C_{10}-N,N-Dialkylacrylamid, C_1-C_{10}-N-Alkylmethacrylamid, C_1-C_{10}-N,N-Dialkylmethacrylamid, N-Arylacrylamid, N,-N-Diarylacrylamid, N-Arylmethacrylamid, N-N-Diarylmethacrylamid, N-Arylalkylacrylamid, N, N-Diallylalkylacrylamid, N-Arylalkylmethacrylamid, N,N-Diarylalkylmethacrylamid, Maleinsäureanhydrid, Itaconsäure, Vinylsulfonsäure, Styrolsulfonsäure, Natriumacrylamidomethylpropansulfonsäure, Maleinsäure und Kombinationen hiervon besteht, erhältliches Copolymer, wobei das Copolymer in einer wäßrigen Salzlösung dispergiert ist.

7. Wäßrige Dispersion nach Anspruch 6, **dadurch gekennzeichnet, daß** das wasserlösliche Copolymer umfaßt:

a) 5 bis 50 Gew.% eines wasserlöslichen Copolymers, das durch Polymerisieren von

i. 1-99 Mol% des N-Vinylamidmonomers und

ii. 99-1 Mol% von mindestens einem der zweiten Vinylmonomeren

unter freie Radikale bildenden Bedingungen bei einem pH-Wert von 5 bis 8 hergestellt wurde;

b) 0,1 bis 5 Gew.% auf der Basis des Gesamtgewichtes der Dispersion eines wasserlöslichen Stabilisatorpolymers mit einer inneren Viskosität in 1M $NaNO_3$ von 0,1-10 dl/g;

c) 5 bis 40 Gew.% auf der Basis des Gewichtes der Dispersion eines wasserlöslichen Salzes; und

d) Wasser,

wobei die Dispersion **dadurch gekennzeichnet ist, daß** sie eine Brookfield-Volumenviskosität von $1x10^{-2}$ Pas (10 cps) bis 25 Pas (25.000 cps) bei 25 °C besitzt.

8. Verfahren zur Herstellung einer wäßrigen Dispersion von getrennten Partikeln des wasserlöslichen Copolymers nach Anspruch 4, **dadurch gekennzeichnet, daß** es die folgenden Schritte umfaßt:

Polymerisieren unter freie Radikale bildenden Bedingungen bei einem pH von 5 bis 8 von

a) 5-50 Gew.% eines Gemisches enthaltend

I. 1-99 Mol% des Vinylamidmonomers und

ii. 99-1 Mol% von mindestens einem wasseriösiichen Vinylmonomer;

b) 0,1 bis 5 Gew.% auf der Basis des Gesamtgewichtes der Dispersion eines wasseriöslichen Stabiiisatorpolymers mit einer inneren Viskosität in 1M $NaNO_3$ von 0,1-10 dl/g;

c) 5 bis 40 Gew.% auf der Basis des Gesamtgewichtes der Dispersion eines wasserlösiichen Salzes; und

d) Wasser,

und dann Gewinnen einer Dispersion des wasseriöslichen Copolymers, die **dadurch gekennzeichnet ist, daß** sie eine Viskosität von weniger ais 25 Pas (25.000 cps) bei 25 °C besitzt.

9. Verfahren zum Herstelien einer wäßrigen Dispersion von getrennten Partikein des wasserlösiichen nichtionischen Homopolymers nach Anspruch 2, **dadurch gekennzeichnet, daß** es die folgenden Schritte umfaßt:

Poiymerisieren unter freie Radikaie biidenden Bedingungen bei einem pH von 5 bis 8 von

a) 5 bis 50 Gew.% eines wasseriösiichen Poiymers, das durch Poiymerisieren eines N-Vinyiamidmonomers der Formel $H_2C=CR^2NRC(O)R^1$ erhäitiich ist, wobei R, R^1 und R^2 jeweils aus der Gruppe ausgewählt sind, die aus Wasserstoff, C_1-C_{20}-Alkyigruppen, Aryigruppen und Arylaikyigruppen besteht;

b) 0,1 bis 5 Gew.% auf der Basis des Gesamtgewichtes der Dispersion eines wasserlöslichen Stabiiisatorpolymers mit einer inneren Viskosität in 1M $NaNO_3$ von 0,1-10 dl/g;

c) 5 bis 40 Gew.% auf der Basis des Gewichtes der Dispersion eines wasseriöslichen Salzes; und

d) Wasser,

und dann Gewinnen einer Dispersion des wasserlöslichen Homopolymers, die **dadurch gekennzeichnet ist, daß** sie eine Brookfieid-Volumenviskosität von $1x10^{-2}$ Pas (10 cps) bis 25 Pas (25.000 cps) bei 25 °C besitzt.

10. Verfahren zur Hersteliung einer wäßrigen Dispersion von getrennten Partikeln des wasserlöslichen Copoyimers nach Anspruch 6, **dadurch gekennzeichnet, daß** es die folgenden Schritte umfaßt:

Polymerisieren unter freie Radikaie biidenden Bedingungen bei einem pH von 5 bis 8 von:

a) 5-50 Gew.% eines Gemisches enthaitend

i. 1-99 Mol% des N-Vinylamidmonomers und

ii. 99-1 Moi-% von mindestens einem der zweiten Vinylmonomeren;

b) 0,1 bis 5 Gew.% auf der Basis des Gesamtgewichtes der Dispersion eines wasseriöslichen Stabilisatorpolymers mit einer inneren Viskosität in 1M $NaNO_3$ von 0,1-10 dl/g;

c) 5 bis 40 Gew.% auf der Basis des Gewichtes der Dispersion eines wasseriösiichen Salzes; und

d) Wasser,

und dann Gewinnen einer Dispersion des wasseriösiichen Copolymers, die **dadurch gekennzeichnet ist, daß** sie eine Brookfield-Volumenviskosität von $1x10^{-2}$ Pas (10 cps) bis 25 Pas (25.000 cps) bei 25 °C besitzt.

11. Dispersion nach den Ansprüchen 1-10, **dadurch gekennzeichnet, daß** das Polymer in einer wäßrigen Saizlösung dispergiert ist, wobei die wäßrige anionische Saizlösung mit einem Salz gebildet ist, das aus der Gruppe ausgewählt ist, die aus Ammonium-, Aikalimetail- und Erdaikalimetail-Haiogeniden, -sulfaten, -phosphaten, -nitraten und Kombinationen hiervon besteht.

12. Dispersion nach Anspruch 1 und 2, **dadurch gekennzeichnet, daß** sie des weiteren ein Stabilisatorpoiymer umfaßt, das aus der Gruppe ausgewähit ist, die aus Poly(vinylalkohol), teilweise hydroiisiertem Poly(vinylacetat), hydrolisiertem Poly(vinyiacetat/N-vinyiformamid), Poly-(vinylaikohol/acryiamid), Poiy(diailyidimethylammoniumchlorid), Poiy (quaternärem Dimethylaminoethylacrylatmethylchioridsaiz), Poiy(quaternärem Dimethylaminoethyimethacrylatmethylchioridsalz), Poly(quaternärem Dimethylaminoethylacrylatbenzyichioridsaiz), Poly(quaternärem Dimethylaminoethylmethacryiatbenzylchöridsalz), Poly (quaternärem Diallyldimethyiammoniumchiorid/dimethyiaminoethyiacrylatmethylchoridsalz), Poly

(quaternärem Diallyldimethylammoniumchlorid/dimethylaminoethylmethacrylatmethylchloridsalz), Poly(quaternärem Diallyldimethylammoniumchlorid/dimethylaminoethylacrylatbenzylchloridsalz) und Poly(quaternärem Diallyldimethylammoniumchlorid/dimethylaminoethylmethacrylatbenzylchloridsalz) und Kombinationen hiervon besteht.

13. Dispersion nach einem der Ansprüche 3-10, **dadurch gekennzeichnet, daß** das Stabilisatorpolymer aus der Gruppe ausgewählt ist, die aus Poly (vinylalkohol), teilweise hydrolisiertem Poly(vinylacetat), hydrolisiertem Poly(vinylacetat/N-vinylformamid), Poly(vinylalkohol/acrylamid), Poly(diallyldimethylammoniumchlorid), Poly(quaternärem Dimethylaminoethylacrylatmethylchloridsalz), Poly (quaternärem Dimethylaminoethylmethacrylatmethylchloirddalz), Poly(quaternärem Dimethylaminoethylacrylatbenzylchloridsalz), Poly(quaternärem Dimethylaminoethylmethacrylatbenzylchloridsalz), Poly(quaternärem Diallyldimethylammoniumchlorid/dimethylaminoethylacrylatmethylchloridsalz), Poly(quaternärem Diallyldimethylammoniumchlorid/dimethylaminoethylmethacrylatmethylchloridsalz), Poly(quaternärem Diallyldimethylammoniumchlorid/ dimethylaminoethylacrylatbenzylchloridsalz) und Poly(quaternärem Diallyldimethylammoniumchlorid/dimethylaminoethylmethacrylatbenzylchloridsalz) und Kombinationen hiervon besteht.

14. Verfahren zur in-situ-Hydrolyse einer Dispersion von getrennten Partikeln des wasserlöslichen Polymers nach Anspruch 1, **dadurch gekennzeichnet, daß** das Polymer hängende Amidgruppen besitzt und in einer wäßrigen Salzlösung dispergiert ist, wobei das Verfahren die folgenden Schritte umfaßt:

a) Rühren der Dispersion;

b) Erhitzen der gerührten Dispersion auf eine Temperatur von 70 °C bis 90 °C;

c) Blasen von HCl-Gas durch die erhitzte Dispersion; und

d) Gewinnen einer Dispersion von getrennten Partikeln eines wasserlöslichen Polymers mit hängenden Amingruppen.

15. Verfahren zur In-situ-Hydrolyse einer Dispersion von getrennten Partikeln eines Copolymers nach Anspruch 6, **gekennzeichnet durch** die folgenden Schritte:

a) Rühren der Dispersion;

b) Erhitzen der gerührten Dispersion auf eine Temperatur von 70 °C bis 90 °C;

c) Blasen von HCl-Gas **durch** die erhitzte Dispersion; und

d) Gewinnen einer Dispersion von getrennten Partikeln eines wasserlöslichen Polymers mit hängenden Amingruppen.

16. Verfahren zum Klären von Abwasser, **dadurch gekennzeichnet, daß** es den Schritt des Zusetzens einer wasserlöslichen, nichtionischen Dispersion nach Anspruch 2 umfaßt, wobei die Dispersion aus getrennten Partikeln eines wasserlöslichen, nichtionischen Poly(N-vinylamid)polymers erhältlich ist durch die Polymerisation eines N-Vinylamidmonomers der Formel

$$H_2C=CR^2NRC(O)R^1$$

worin R, R^1 und R^2 jeweils aus der Gruppe ausgewählt sind, die aus Wasserstoff, C_1-C_{20}-Alkylgruppen, Arylgruppen und Alkylaryl besteht, zum Abwasser umfaßt.

17. Verfahren zum Entwässern von Abwasser, **dadurch gekennzeichnet, daß** es den Schritt des Zusetzens der wasserlöslichen, nichtionischen Dispersion nach Anspruch 2 zum Abwasser umfaßt, wobei die Dispersion von getrennten Partikeln eines wasserlöslichen, nichtionischen Poly(N-vinylamid)polymers durch Polymerisation eines Vinylamidmonomers der Formel

$$H_2C=CR^2NRC(O)R^1$$

erhältlich ist, wobei R, R^1 und R^2 jeweils aus der Gruppe ausgewählt sind, die aus Wasserstoff, C_1-C_{20}-Alkylgruppen, Arylgruppen und Alkylaryl besteht.

18. Verfahren zum Klären von Abwasser, **dadurch gekennzeichnet, daß** es den Schritt des Zusetzens der wasserlöslichen Dispersion nach Anspruch 4 zum Abwasser umfaßt, wobei das Copolymer in einer wäßrigen Salzlösung dispergiert ist.

19. Verfahren zum Entwässern von Abwasser, **dadurch gekennzeichnet, daß** es den Schritt des Zusetzens der wasserlöslichen Dispersion nach Anspruch 4 zum Abwasser umfaßt, wobei das Copolymer in einer wäßrigen Salzlösung dispergiert ist.

20. Verfahren zum Klären von Abwasser, **dadurch gekennzeichnet, daß** es den Schritt des Zusetzens der wasserlöslichen Dispersion nach Anspruch 6

zum Abwasser umfaßt, wobei das Copolymer in einer wäßrigen Salzlösung dispergiert ist.

21. Verfahren zum Entwässern von Abwasser, **dadurch gekennzeichnet, daß** es den Schritt des Zusetzens der wasserlöslichen, nichtionischen Dispersion nach Anspruch 6 zum Abwasser umfaßt, wobei das Copolymer in einer wäßrigen Salzlösung dispergiert ist.

22. Verfahren nach einem der Ansprüche 16-21, **dadurch gekennzeichnet, daß** das Abwasser aus der Gruppe ausgewählt ist, die aus industriellem Abwasser, industriellem Prozeßwasser und städtischem Abwasser besteht.

23. Verfahren nach Anspruch 22, **dadurch gekennzeichnet, daß** das industrielle Abwasser aus der Gruppe ausgewählt ist, die aus Nahrungsmittelbehandlungsabwasser, öligem Abwasser, Papierfabrikabwasser und Abwasser der Montanindustrie besteht.

Revendications

1. Dispersion aqueuse, **caractérisée en ce qu'**elle comprend des particules discrètes d'un polymère non ionique hydrosoluble pouvant être obtenu par la polymérisation de monomères, lesdits monomères comprenant des monomères de N-vinylamide ayant la formule suivante :

$$H_2C=CR^2NRC(O)R^1$$

dans laquelle R, R^1 et R^2 sont chacun choisis dans le groupe constitué par l'hydrogène, des groupes alkyle en C_1-C_{20}, des groupes aryle et des groupes alkylaryle.

2. Dispersion selon la revendication 1, **caractérisée en ce que** ledit polymère est un homopolymère de poly(N-vinylamide) non ionique et ledit monomère de N-vinylamide est choisi dans le groupe constitué par le N-vinylformamide, le N-méthyl-N-vinylacétamide et le N-vinylacétamide.

3. Dispersion aqueuse de particules discrètes de l'homopolymère hydrosoluble non ionique de la revendication 2, **caractérisée en ce qu'**elle comprend:

a) 5 à 50 pour-cent en poids d'un polymère hydrosoluble pouvant être obtenu par polymérisation dans des conditions de formation de radicaux libres à une valeur de pH de 5 à environ 8, d'un monomère N-vinylformamide ;
b) 0,1 à 5 pour-cent en poids rapporté au poids total de la dispersion d'un polymère stabilisant hydrosoluble ayant une viscosité intrinsèque dans $NaNO_3$ 1 M de 0,1-10 dl/g;
c) 5 à 40 pour-cent en poids rapporté au poids de la dispersion d'un sel hydrosoluble ; et
d) de l'eau,

ladite dispersion étant **caractérisée en ce qu'**elle présente une viscosité apparente Brookfield de 1 x 10^{-2} Pas (10 cps) à 25 Pas (25 000 cps) à 25°C.

4. Dispersion aqueuse de particules discrètes du polymère hydrosoluble de la revendication 1, **caractérisée en ce que** ledit polymère est un copolymère comprenant :

un copolymère pouvant être obtenu par polymérisation d'un monomère N-vinytamide de formule :

$$H_2C=CR^2NRC(O)R^1$$

dans laquelle R, R^1 et R^2 sont chacun choisis dans le groupe constitué par l'hydrogène, des groupes allyle en C_1-C_{20}, des groupes aryle et des groupes alkylaryle ; avec au moins un second monomère choisi dans le groupe constitué par l'acétate de vinyle, le chlorure de diallyidiméthylammonium, la vinylpyrrolidone, l'acrylonitrile, le sel quaternaire de chlorure de diméthylaminoéthylacrylate de méthyle, le sel quaternaire de chlorure de diméthylaminoéthylacrylate de benzyle, le sel quaternaire de sulfate de diméthylaminoèthylacrylate de méthyle, le sel quaternaire de chlorure de diméthylaminoéthylacrylate de cétyle, le sel quaternaire de diméthylaminoéthylméthacrylate de cétyle, le sel quaternaire de chlorate de diméthylaminoéthylméthacrylate de méthyle, le sel quaternaire de chlorure de diméthylaminoéthylméthacrylate de benzyle, le sel quaternaire de sulfate de diméthylaminoéthylméthacrylate de méthyle, et leurs combinaisons ; ledit copolymère étant dispersé dans une solution saline aqueuse.

5. Dispersion aqueuse de la revendication 4, **caractérisée en ce que** ladite dispersion comprend:

a) 5 à 50 pour-cent en poids d'un copolymère hydrosoluble pouvant être obtenu en polymérisant à un pH de 5 à 8 :

i. 1 - 99 pour-cent en moles dudit monomère N-vinylamide
ii. 99 - 1 pour-cent en mole d'au moins un desdits seconds monomères

b) 0,1 à 5 pour-cent en polds rapporté au poids total de la dispersion d'un polymère stabilisant hydrosoluble ayant une viscosité intrinsèque dans $NaNO_3$ 1 M de 0,1 - 10 dl/g ;
c) 5 à 40 pour-cent en poids rapporté au poids de la dispersion d'un sel hydrosoluble ; et
d) de l'eau,

ladite dispersion élant **caractérisée en ce qu'**elle présente une viscosité apparente Brookfield de 1 x 10^{-2} Pas (10 cps) à 25 Pas (25 000 cps) à 25°C.

6. Dispersion aqueuse de particules discrètes d'un polymère hydrosoluble de la revendication 1, **caractérisée en ce que** ledit polymère est un copolymère comprenant un copolymère pouvant être obtenu par polymérisation d'un monomère N-vinylamide de formule :

$$H_2C=CR^2NRC(O)R^1$$

dans laquelle R, R^1 et R^2 sont chacun choisis dans le groupe constitué par l'hydrogène, des groupes alkyle en C_1-C_{20}, des groupes aryle et des groupes alkylaryle ;

avec au moins un second monomère choisi dans le groupe constitué par l'acide acrylique et ses sels, le méthacrylamide et ses sels, un N-alkyl(en C_1-C_{10})acrylamide, un N,N-dialkyl(en C_1-C_{10}) acrylamide, un N-alkyl(en C_1-C_{10})méthacrylamide, un N,N-dialkyl(en C_1-C_{10})méthacrylamide, le N-arylacrytamide, un N,N-diarylacrylamide, un N-arylméthacrylamide, le N,N-diarylméthacrylamide, un N-arylalkylacrylamide, un N,N-diallylalkylacrylamide, un N-arylalkylméthacrylamide, un N,N-diarylalkylméthacrylamide, l'anydride maléique, l'acide itaconique, l'acide vinylsulfonique, l'acide styrènesulfbnique, l'acide acrylamidométhylpropanesulfonique sodique, l'acide maléique et leurs combinaisons, ledit copolymère étant dispersé dans une solution saline aqueuse.

7. Dispersion aqueuse de la revendication 6, **caractérisée en ce que** ledit copolymère hydrosoluble comprend :

a) 5 à 50 pour-cent en poids d'un copolymère hydrosoluble ayant été préparé en polymérisant dans des conditions de formation de radicaux libres à une valeur de pH de 5 à 8 :

i. 1 - 99 pour-cent en moles dudit monomère N-vinylamide
ii. 99 - 1 pour-cent en moles d'au moins un desdits seconds monomères vinyliques

b) 0,1 à 5 pour-cent en poids rapporté au poids total de la dispersion d'un polymère stabilisant hydrosoluble ayant une viscosité intrinsèque dans $NaNO_3$ 1 M de 0,1-10 dl/g ;
c) 5 à 40 pour-cent en poids rapporté au poids de la dispersion d'un sel hydrosoluble
d) de l'eau,

ladite dispersion étant **caractérisée en ce qu'**elle présente une viscosité apparente Brookfield de 1 x 10^{-2} Pas (10 cps) à 25 Pas (25 000 cps) à 25°C.

8. Procédé de préparation dune dispersion aqueuse de particules discrètes dudit copolymère hydrosoluble de la revendication 4, **caractérisé en ce qu'**il comprend les étapes consistant à :

polymériser dans des conditions de formation de radicaux libres à un pH de 5 à 8 :

a) 5 - 50 pour-cent en poids d'un mélange contenant

i. 1 - 99 pour-cent en moles dudit monomère vinylamide
ii. 99 - 1 pour-cent en moles d'au moins un d'un monomère vinylique hydrosoluble

b) 0,1 à 5 pour-cent en poids rapporté au poids total de la dispersion d'un polymère stabilisant hydrosoluble ayant une viscosité intrinsèque dans $NaNO_3$ 1 M de 0,1 - 10 dl/g ;
c) 5 à 40 pour-cent en poids rapporté au poids de la dispersion d'un sel hydrosoluble ; et
d) de l'eau,

et ensuite récupérer une dispersion dudit copolymère hydrosoluble, ladite dispersion étant **caractérisée en ce qu'**elle présente une viscosité inférieure à 25 Pas (25 000 cps) à 25°C.

9. Procédé de préparation d'une dispersion aqueuse de particules discrètes dudit homopolymère non ionique hydrosoluble de la revendication 2, **caractérisé en ce qu'**il comprend les étapes consistant à polymériser dans des conditions de formation de radicaux libres à un pH de 5 à 8 :

a) 5 à 50 pour-cent en poids d'un polymère hydrosoluble pouvant être obtenu en polymérisant un monomère N-vinylamide de formule

$$H_2C=CR^2NEC(O)R^1$$

dans laquelle R, R^1 et R^2 sont chacun choisis

dans le groupe constitué par l'hydrogène, des groupes alkyle en C_1-C_{20}, des groupes aryle et des groupes alkylaryle ;
b) 0,1 à 5 pour-cent en poids rapporté au poids total de la dispersion d'un polymère stabilisant hydrosoluble ayant une viscosité Intrinsèque dans $NaNO_3$ 1 M de 0,1 - 10 dl/g;
c) 5 à 40 pour-cent en poids rapporté au poids de la dispersion d'un sel hydrosoluble; et
d) de l'eau,

et ensuite récupérer une dispersion dudit homopolymère hydrosoluble, ladite dispersion étant **caractérisée en ce qu**'elle présente une viscosité apparente Brookfield de 1 x 10^{-2} Pas (10 cps) à 25 Pas (25 000 cps) à 25°C.

10. Procédé de préparation dune dispersion aqueuse de particules discrètes dudit copolymère hydrosoluble de la revendication 6, **caractérisé en ce qu**'il comprend les étapes consistant à polymériser dans des conditions de formation de radicaux libres à un pH de 5 à 8 :

a) 5 - 50 pour-cent en poids d'un mélange contenant

i. 1 - 99 pour-cent en moles dudit monomère N-vinylamide
ii. 99 - 1 pour-cent en moles d'au moins un desdits seconds monomères vinyliques

b) 0,1 à 5 pour-cent en poids rapporté au poids total de la dispersion d'un polymère stabilisant hydrosoluble ayant une viscosité intrinsèque dans $NaNO_3$ 1 M de 0,1 - 10 dl/g ;
c) 5 à 40 pour-cent en poids rapporté au poids de la dispersion d'un sel hydrosoluble ; et
d) de l'eau,

et ensuite récupérer une dispersion dudit copolymère hydrosoluble, ladite dispersion étant **caractérisée en ce qu**'elle présente une viscosité apparente Brookfield de 1 × 10^{-2} Pas (10 cps) à 25 Pas (25 000 cps) à 25°C.

11. Dispersion selon les revendications 1 - 10, **caractérisée en ce que** ledit polymère est dispersé dans une solution aqueuse de sel ; dans laquelle ladite solution aqueuse anionique de sel est formée avec un sel cholsi dans le groupe constitué par des halogénures, sulfates, phosphates, nitrates d'ammonium, de métaux alcalins et de métaux alcalinoterreux, et leurs combinaisons.

12. Dispersion selon les revendications 1 et 2, **caractérisée en ce que** ladite dispersion comprend en outre un polymère stabilisant, dans laquelle ledit polymère stabilisant est choisi dans le groupe constitué par le poly(alcool vinylique), le poly(acétate de vinyle) partiellement hydrolysé, le poly(acétate de vinyle/N-vinylformamide) hydrolysé, le poly(alcool vinylique/acrylamide), le poly(chlorure de diallyldiméthylammonium), le poly(sel quaternaire de chlorure de diméthylaminoéthylacrylate de méthyle), le poly(sel quatemaire de chlorure de diméthylaminoéthylméthacrylate de méthyle), le poly(sel quaternaire de chlorure de diméthylaminoéthylacrylate de benzyle), le poly(sel quaternaire de chlorure de diméthylaminoéthylméthacrylate de benzyle), le poly(sel quaternaire de chlorure de diallyldiméthylammonium/chlorure de diméthylaminoéthylacrylate de méthyle), le poly(sel quaternaire de chlorure de diallyldiméthylammonium/chlorure de diméthylaminoéthylméthacrylate de méthyle), le poly(sel quaternaire de chlorure de diallyldiméthylammonium/chlorure de diméthylaminoéthylacrylate de benzyle), et le poly(sel quaternaire de chlorure de diallyldiméthylammonium/chlorure de diméthylaminoéthylméthacrylate de benzyle) et leurs combinaisons.

13. Dispersion selon l'une quelconque des revendications 3 - 10, **caractérisée en ce que** ledit polymère stabilisant est choisi dans le groupe constitué par le poly(alcool vinylique), le poly(acétate de vinyle) partiellement hydrolysé, le poly(acétate de vinyle/N-vinylformamide) hydrolysé, le poly(alcool vinylique/acrylamide), le poly(chlorure de diallyldiméthylammonium), le poly(sel quaternaire de chlorure de diméthylaminoéthylacrylate de méthyle), le poly(sel quaternaire de chlorure de diméthylaminoéthylméthacrylate de méthyle), le poly(sel quatemaire de chlorure de diméthylaminoéthylacrylate de benzyle), le poly(sel quatemaire de chlorure de dimethylaminoéthylméthacrylate de benzyle), le poly(sel quaternaire de chlorure de diallyldiméthylammonium/chlorure de diméthylaminoéthylacrylate de méthyle), le poly(sel quaternaire de chlorure de diallyldiméthylammonium/chlorure de dimethylaminoéthylméthacrylate de méthyle), le poly(sel quatemaire de chlorure de diallyidiméthylammonium/chlorure de diméthylaminoéthylacrylate de benzyle), et le poly(sel quaternaire de chlorure de diailyldiméthylammonium/chlorure de diméthylaminoéthylméthacrylate de benzyle) et leurs combinaisons.

14. Procédé pour l'hydrolyse in situ d'une dispersion de particules discrètes du polymère hydrosoluble de la revendication 1, **caractérisé en ce que** ledit polymère présente des groupes amides pendants, ledit polymère dispersé dans une solution aqueuse de sel comprenant les étapes consistant à:

a) agiter ladite dispersion ;

b) chauffer ladite dispersion agitée à une température de 70°C à 90°C;
c) faire barboter du gaz HCl à travers ladite dispersion chauffée ; et,
d) récupérer une dispersion de particules discrètes d'un polymère hydrosoluble ayant des groupes amines pendants.

15. Procédé pour l'hydrolyse in situ dune dispersion de particules discrètes du copolymère hydrosoluble de la revendication 6, **caractérisé en ce qu'**il comprend les étapes consistant à :

a) agiter ladite dispersion ;
b) chauffer ladite dispersion agitée à une température de 70°C à 90°C ;
c) faire barboter du gaz HCl à travers ladite dispersion chauffée ; et,
d) récupérer une dispersion de particules discrètes d'un polymère hydrosoluble ayant des groupes amines pendants.

16. Procédé pour clarifier des eaux usées, **caractérisé en ce qu'**il comprend l'étape consistant à ajouter auxdites eaux usées la dispersion non ionique hydrosoluble de la revendication 2, ladite dispersion de particules discrètes d'un polymère non ionique hydrosoluble de poly(N-vinylamide) pouvant être obtenue par polymérisation d'un monomère de N-vinylamide de formule :

$$H_2C=CR^2NRC(O)R^1$$

dans laquelle R, R^1 et R^2 sont chacun choisis dans le groupe constitué par l'hydrogène, des groupes alkyle en C_1-C_{20}, des groupes aryle et des groupes alkylaryle.

17. Procédé pour éliminer l'eau des eaux usées, **caractérisé en ce qu'**il comprend l'étape consistant à ajouter auxdites eaux usées la dispersion non ionique hydrosoluble de la revendication 2, ladite dispersion de particules discrètes d'un polymère non ionique hydrosoluble de poly(N-vinylamide) pouvant être obtenue par polymérisation d'un monomère de vinylamide de formule :

$$H_2C=CR^2NRC(O)R^1$$

dans laquelle R, R^1 et R^2 sont chacun choisis dans le groupe constitué par l'hydrogène, des groupes alkyle en C_1-C_{20}, des groupes aryle et des groupes alkylaryle.

18. Procédé pour clarifier des eaux usées, **caractérisé en ce qu'**il comprend l'étape consistant à ajouter auxdites eaux usées la dispersion hydrosoluble de la revendication 4, ledit copolymère étant dispersé dans une solution aqueuse de sel.

19. Procédé pour éliminer l'eau des eaux usées, **caractérisé en ce qu'**il comprend l'étape consistant à ajouter auxdites eaux usées la dispersion hydrosoluble de la revendication 4, ledit copolymère étant dispersé dans une solution aqueuse de sel.

20. Procédé pour clarifier des eaux usées, **caractérisé en ce qu'**il comprend l'étape consistant à ajouter auxdites eaux usées la dispersion hydrosoluble de la revendication 6, ledit copolymère étant dispersé dans une solution aqueuse de sel.

21. Procédé pour éliminer l'eau des eaux usées, **caractérisé en ce qu'**il comprend l'étape consistant à ajouter auxdites eaux usées la dispersion hydrosoluble de la revendication 6, ledit copolymère étant dispersé dans une solution aqueuse de sel.

22. Procédé selon l'une quelconque des revendications 16 - 21, **caractérisé en ce que** lesdites eaux usées sont choisies dans le groupe constitué par des eaux usées industrielles, des eaux de procédés industriels et des eaux usées municipales.

23. Procédé selon la revendication 22, **caractérisé en ce que** lesdites eaux usées industrielles sont choisies dans le groupe constitué par des eaux usées de traitement alimentaire, des eaux usées huileuses, des eaux usées d'usines à papier, et des eaux usées de mines.